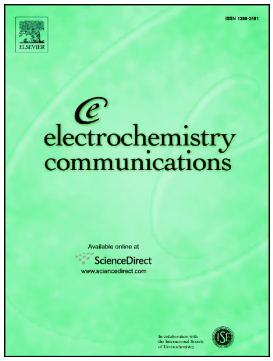

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Copper underpotential deposition at gold surfaces in contact with a deep eutectic solvent: New insights

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ABSTRACT

The electrodeposition of copper on a polycrystalline gold electrode and on Au(hkl) single crystals was investigated in a deep eutectic solvent (DES). The DES employed consisted of a mixture of choline chloride and urea (1:2). The Au(hkl)/DES interface was studied using cyclic voltammetry in the capacitive region. The blank voltammograms showed characteristic features, not previously reported, that demonstrate the surface sensitivity of this solvent. Copper electrodeposition was then studied and it was found that this takes place through the formation of an underpotential deposition (UPD) adlayer, demonstrating the surface sensitivity of this process. Voltammetric profiles showed similarities with those obtained in aqueous solutions containing chloride, suggesting that the copper UPD in this DES is strongly influenced by the presence of chloride.

KEY WORDS

Single crystal; deep eutectic solvent; interface; underpotential deposition; chloride.

INTRODUCTION

Since it was discovered that ionic liquids (ILs) are effective solvents, their use in electrochemical processes has been widespread [1, 2]. The instability of the early forms of these liquids has been overcome in the search for air and water stable ILs. Among these, deep eutectic solvents (DESs) are often used because they are both environmentally friendly and relatively cheap. These room temperature ionic liquids are prepared by mixing a hydrogen-bond donor with a quaternary ammonium salt [1, 3-9].

Given their excellent ability to solvate metal ions, DESs have been widely employed in electrodeposition processes. Different aspects of the prepared coatings have been studied: morphology, stress, corrosion, even the first stages of the deposition process [10-18]. However, very few studies have been devoted to the interaction of solvent molecules with the electrode surface and the possible effect of this interaction on the electrodeposition process [19, 20]. In this work, the deposition of copper on gold from a DES composed of a urea:choline chloride (2:1 molar ratio) has been studied, focusing on the interaction between the components of the solution and the substrate. Both polycrystalline and single crystal gold electrodes were employed and the Au(hkl)|DES interface was investigated.

EXPERIMENTAL

Working electrodes were prepared from single crystal beads, as reported elsewhere [21]. The polycrystalline sample was a polyoriented single crystal bead, Au(poly). A Cu wire was used as the reference electrode and a gold wire as the counter electrode. The potentials were further referred to the Ag|AgCl|3M KCl reference electrode. All working electrodes were flame-annealed and cooled to the ambient temperature in argon before immersion in the cell. The electrochemical experiments were performed in a small volume cell and controlled by a μ-Autolab instrument (Eco-Chemie, Ultrecht, The Netherlands). The temperature of all the experiments was kept at 40°C using a thermostatted bath.

Urea (Merck p.a.) and choline chloride (Across, 99%) were mixed (molar rate 2:1) at a low temperature (T < 40°C). Before the experiment, the DES was kept under vacuum (P < 0.002 mbar) and at 30°C overnight under stirring [22]. CuCl and $CuCl_2$ (p.a. quality) were also purchased from Merck.

RESULTS AND DISCUSION

A detailed voltammetric study of the capacitive potential region between -0.95 and 0.40 V vs Ag|AgCl was performed on Au(poly), revealing singular features of the Au(poly)|DES interface (Figure 1A). The voltammogram shows a capacitive current (capacity around 50 μF cm^{-2}) that increases linearly with the scan rate. Overlapping this capacitive current, a few broad peaks (w, a and b) and one small, quite sharp peak (c) appear in the positive scan. The counter peaks also appear in the reverse scan, demonstrating quasi-reversible behavior. The lack of perfect reversibility can be ascribed to the high viscosity and low mobility of ions in solution. The

appearance of these peaks is most likely related to 2D phase transitions involving the species of the electrolyte. In particular, the sharp peaks have been ascribed to phase transitions in the anion adlayer, and were previously reported in aqueous solution [23-25] and recently in the [Emmim][Tf_2N] room temperature ionic liquid [26]. It should be noted that the concentration of chloride in the solvent is around 4.8M [27, 28], so a strong effect from chloride adsorption is expected. The low current intensity of these peaks is due to the small size of the corresponding facets of the Au bead. Single crystal electrodes were therefore employed to explore this capacitive region in more detail. Figures 1B and 1C show the cyclic voltammograms obtained with Au(111) and Au(100) in contact with the DES. As expected, the response is sensitive to the surface structure. For the Au(111) orientation, the group of peaks labelled as a, b and c (Figure 1B) in the positive scan appears at approximately the same potential position as the corresponding peaks for the polycrystalline bead (Figure 1A). There is also a new small peak at higher potentials (d, Figure 1B) not observed on Au(poly). These results show that the voltammetric profile of Au(poly) has a major contribution from the (111) orientation, because these facets are the largest (disordered regions do not contribute sharp peaks). After reversing the scan, a similar group of peaks was found in the negative scan, but the lack of symmetry between positive and negative scans is now more evident, supporting the theory that structuring of the solvent takes place slowly. Other possible contributions to the voltammogram are related to the existence of surface reconstruction, which is strongly linked to anion adsorption as previously observed on Au surfaces in aqueous electrolytes [23]. Cyclic voltammograms were also recorded for Au(100) (Figure 1C), with a profile that differs clearly from the previous one. In the high potential region, a group of quasi-reversible peaks is observed (x, y, z and the counter peaks x', y' and z') while at about -0.25 V vs Ag|AgCl a more prominent peak (w) appears in the positive scan. The latter is also observed for Au(poly), but to a much lesser extent, most likely reflecting the fact that the contribution from the (100) facets is very small in the polyoriented bead. This peak is also similar to that ascribed to the lifting of the hexagonal reconstruction characteristic of (100) surfaces [23, 29]. The counter peak was not clearly identified and two broad peaks (v' and w') were found instead, suggesting that the surface reconstruction is slow and irreversible.

It is important to highlight that all of the cyclic voltammetry recorded between -0.95 and 0.40 V vs Ag|AgCl was stable in consecutive scans, including the results for Au(111), contrary to what has been reported in [Emmim][Tf_2N] [26]. It is evident that the complexity of the voltammetric response reflects the particular nature of the solvent. How the solvent network

is structured in the Au(hkl)|DES interface probably mainly involves the chloride, but the urea and choline also both contribute [30, 31].

Finally, the potential window voltammograms from the blank solution on Au(hkl) and Au(poly) were recorded (Figure 1D), showing a pair of surface-insensitive broad peaks in the negative scan. Similar peaks have been observed for other metal surfaces and assigned to an earlier step in the massive reduction of the solvent. In the positive scan, no relevant oxidation features were recorded before the massive oxidation of the solvent. After attaining the oxidation limit, a reduction peak appears in the reverse scan, which increases on increasing the upper potential limit. In any case, the electrochemical window is not greater than 2.3V, being smaller than that of conventional RTILs (3–5 V) [2].

After measuring the blank response from the solvent, copper electrodeposition was studied, firstly using a poly(Au) electrode. Figure 2 shows the cyclic voltammograms for copper electrodeposition on the gold bead in 10 mM CuCl solution. The Cu(I) state is stabilized by chloride complexation. A quasi-reversible Cu(II)–Cu(I) redox process appears around 0.29 V, well separated from the Cu(I)–Cu electrodeposition [17, 28, 32]. The cyclic voltammogram for Cu(I) electrodeposition shows a rapid increase in the cathodic current with a diffusion-controlled maximum. On reversing the scan, a sharp oxidation peak appears, demonstrating the easy dissolution of the copper deposit, probably because the high chloride concentration in the DES favors it. Interestingly, on reversing the scan at the beginning of the main reduction current the typical nucleation loop does not show [33], suggesting that the initial steps of the copper electrodeposition could involve the formation of one copper sub-monolayer before the nucleation and growth regime is reached [34, 35]. Figure 2B shows the cyclic voltammogram recorded just before the bulk deposition of copper. Around -0.37 and 0.06 V two pairs of peaks (dashed line) appear, which could be related to copper UPD, mainly in the ordered domains. The total charge integrated in the potential region between -0.50 and 0.16 V is ca. 146 $\mu C\ cm^{-2}$ (without subtracting the double layer contribution). On slightly increasing the negative limit (-0.6 V vs Ag|AgCl), a small peak (a) overlaps with the bulk deposition. In the positive scan, a broad oxidation peak (peak a') shifted with respect to the oxidation of bulk copper (b') is observed. The charge integrated in the cathodic scan for peak (a) (between -0.50 and -060 V, without double layer correction) amounts to ca. 140 $\mu C\ cm^{-2}$. A preliminary explanation of these results is that a second monolayer or even a few monolayers could grow layer by layer over the first UPD layer before reaching the growth regime, as previously reported [36]. Moreover, the current density within the potential region between -0.50 and 0.16 V, considered here to be the UPD region, increases linearly with the scan rate (Figure 2C and 2D).

This result shows that the whole process (both the UPD and the minor capacitive contribution) takes place on the surface. Our results therefore support the view that UPD is the step before copper bulk deposition in the DES, since copper UPD was previously reported on gold electrodes in aqueous electrolytes [37] and also in this DES on platinum electrodes [32].

In order to gain more insight into the copper UPD step, single crystals were employed. Figures 3A and 3B show the Cu UPD potential range on Au(111) and Au(100), respectively. The Cu UPD on Au(111) involves two groups of peaks. The first pair of peaks is located at the most positive potentials (0.10 V vs Ag|AgCl), while the other pair is located near the onset of the copper deposition (centered around -0.42 V vs Ag|AgCl). Similar groups of signals were reported in aqueous solutions containing chloride, a medium in which it became clear that the specific nature of the anions affects the UPD process [37, 38]. In sulphate-containing solutions the more positive pair of peaks was assigned to the formation of a ($\sqrt{3}\times\sqrt{3}$) R30° honeycomb [39]. The second pair of peaks was assigned to a full copper monolayer. The presence of chloride shifts the position of the peaks and also affects the reversibility. Moreover, the chloride induces the transformation of the ($\sqrt{3}\times\sqrt{3}$) R30° to a (5×5), corresponding to the first UPD peak, with the chloride ions lying on top of the copper adlayer and forming a bilayer structure lattice [38, 40, 41]. Because chloride interacts strongly with copper, it is expected that the high chloride concentration in the DES plays an important role in the final structure of the UPD adlayers. However, the voltammetric profile that we report here shows a few differences from those previously reported in aqueous solutions, since the two groups of peaks appear more separated in the potential range and show less reversibility. These differences can be attributed to the presence of the other species in the DES (choline and urea), since the addition of organic compounds can modify the UPD region [42-44]. The charge involved within these characteristic UPD peaks (i.e. subtracting a constant pseudo-capacitance value as measured at -0.5 V, 180 $\mu F\ cm^{-2}$) is around 240 $\mu C\ cm^{-2}$, a figure that approaches the corresponding value for a whole copper monolayer (220 $\mu C\ cm^{-2}$), assuming here that the copper deposition only involves the transfer of one electron (Cu(I)–Cu), and neglecting any coulometric contribution from anion adsorption [45].

The cyclic voltammogram for copper UPD on Au(100) shows only a pair of quasi-reversible peaks around 0.142 V vs Ag|AgCl. The corresponding charge for the UPD feature, integrated after subtracting the pseudo-capacitance measured at -0.50 V (70 $\mu F\ cm^{-2}$), is around 130 $\mu C\ cm^{-2}$ (while the total charge for a whole copper monolayer deposited on Au(100) is ca. 190 $\mu C\ cm^{-2}$ [45]).

The profile reported here is very similar to that recorded in chloride-containing aqueous solutions. However, while a sharp peak is observed in the positive scan, the corresponding counter peak splits into a very thin peak overlapped with a broader one in the negative scan. This result provides evidence that the nature of the DES affects the UPD process, although a strong interaction between the copper adlayer and the chloride is also expected [36, 46, 47].

It is worth pointing out that the onset of the UPD process takes place immediately after the first Cu(II)/Cu(I) electron transfer, even when $CuCl_2$ (Cu(II)) is the copper source (not shown), at the potential at which Cu(I) is stabilized (Figure 3C and 3D, dashed lines). This result strongly suggests that copper UPD on a gold electrode in a choline chloride–urea based DES takes place from the stable Cu(I)–chloride complex. From these data it is difficult to know whether the charge involved in the UPD region corresponds only to the Cu(I)–Cu reduction or whether there is also a contribution from the adsorption of one of more of the DES species on the copper adlayer, most likely chloride [41, 48].

Finally, on enlarging the negative scan (Figure 3C and 3D, solid lines), the beginning of copper bulk deposition is observed. While only one oxidation peak appears on Au(111), two oxidation peaks were detected on Au(100)as well as a broader and less prominent peak that extends to the 0.0 V potential limit. These features could be related to the earlier formation of some copper adlayers before the growth regime is reached [36]. Further work is needed to fully understand the phenomenon of metal UPD in DESs.

CONCLUSIONS

Voltammetric experiments were conducted for different Au surfaces in contact with a eutectic mixture of urea and choline chloride (DES), revealing that the interfacial behavior is structure sensitive. Several sharp and characteristic peaks that had not been previously described were observed overlapping the capacitive current recorded for each electrode.

Copper deposition on gold electrodes was also investigated, taking advantage of the fact that Cu(I) solutions can be used. It was found that bulk copper deposition is preceded by the formation of a UPD copper adlayer. Copper UPD on Au(111) and Au(100) showed characteristic sharp peaks and similar profiles to those recorded in chloride-containing aqueous solutions. Chloride is therefore probably involved in the UPD formation. These preliminary results indicate that UPD in the DES takes place from the stabilized Cu(I)–Cl complex.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

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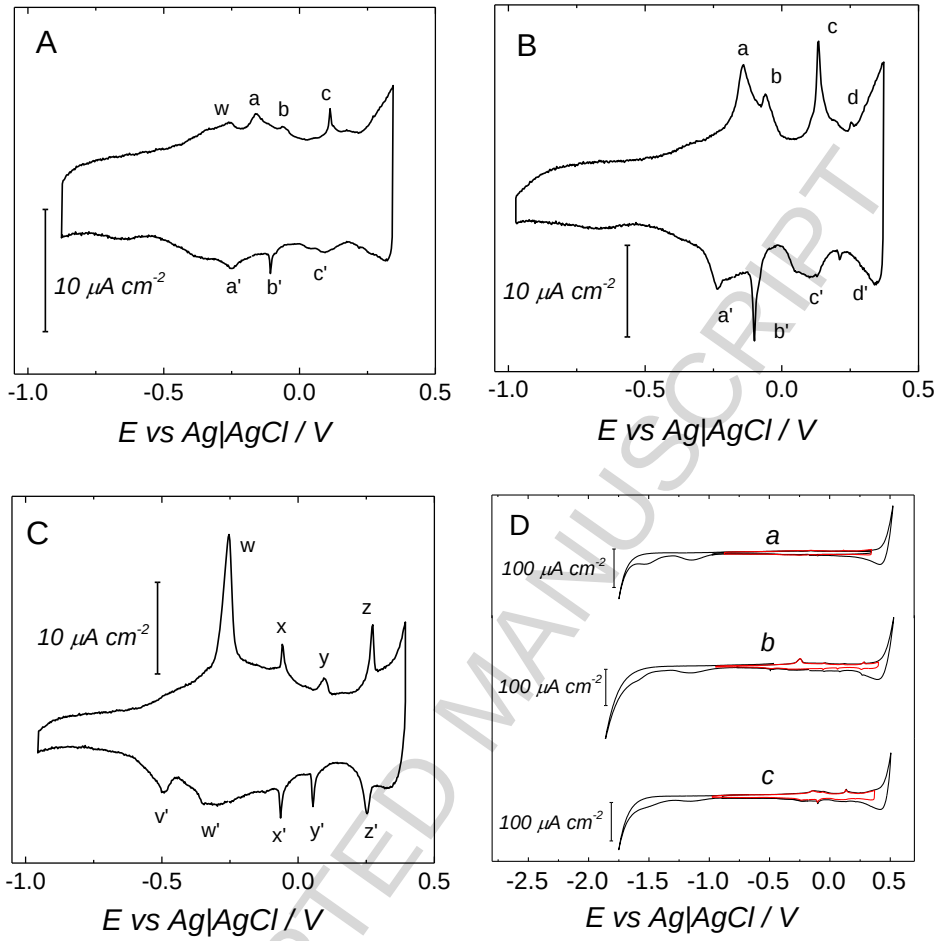

Figure 1. Cyclic voltammograms for (A) Au(poly), (B) Au(111) and (C) Au(100) electrodes in contact with the DES, (D) large potential window voltammograms for (a) Au(poly), (b) Au(100) and (c) Au(111). Scan rate: 50 mV/s.

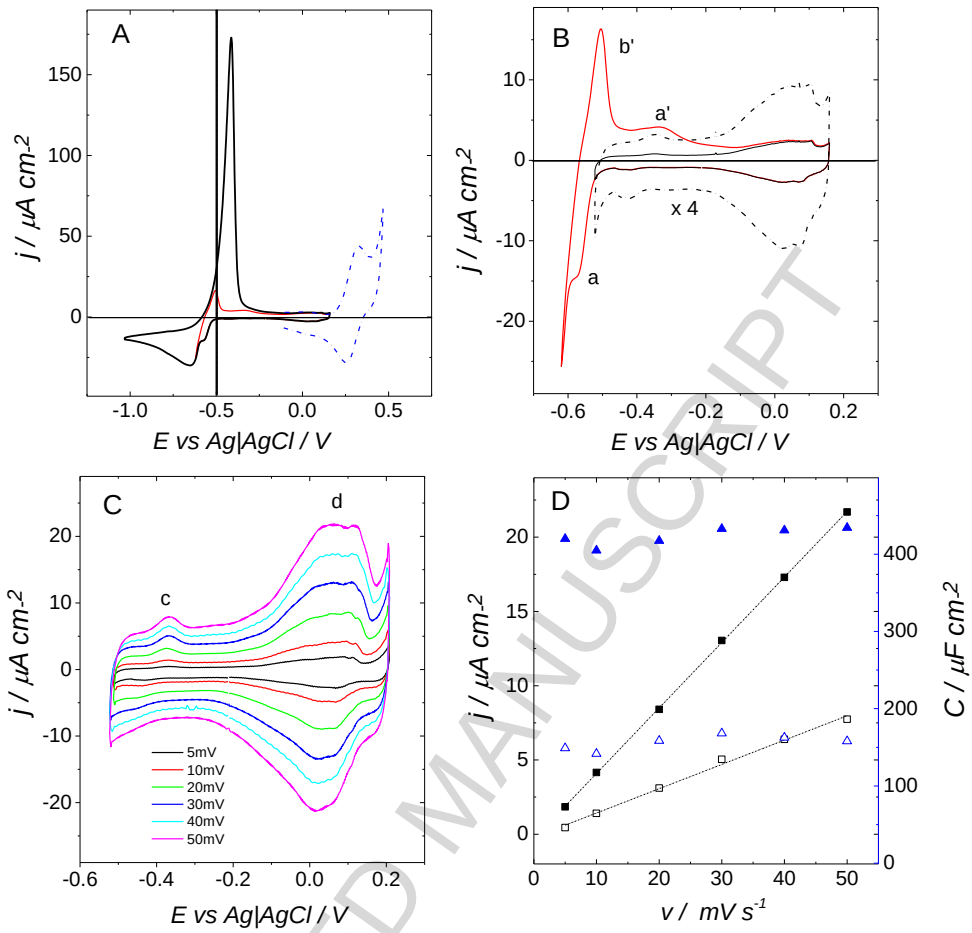

Figure 2. Cyclic voltammograms for copper electrodeposition on Au(poly) from a 10mM CuCl + DES solution: (A) and (B) different potential limits (dashed line in B is just an enlargement of the black curve). Scan rate at 5 mV/s. (C) Copper UPD recorded at different scan rates. (D) Plots of current densities (squares) and pseudocapacitance (*j/v*) (triangles) of the UPD region vs the scan rate. Open and filled symbols correspond to the maximum values measured at peaks *c* and *d* respectively, from Figure 2C. The vertical line in Figure 2A marks the reversible potential for bulk copper deposition.

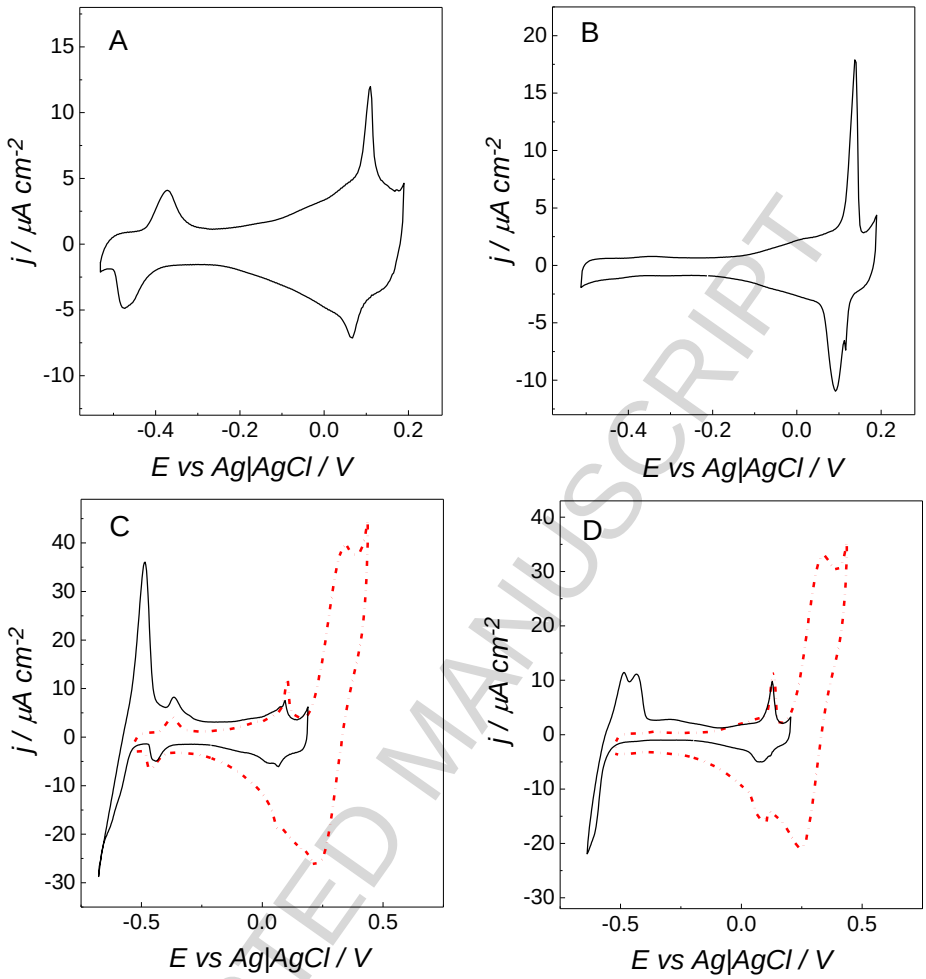

Figure 3. Cyclic voltammograms for Cu UPD deposition on Au(hkl) electrodes, from a 10mM CuCl +DES solution. (A) Au(111), (B) Au(100). Potential limits showing the Cu(II)–Cu(I) reduction (dashed line) and the onset of bulk deposition (solid line) on: (C) Au(111), (D) Au (100). Scan rate: 5mV/s.

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Highlights

- The interface between Au (polycrystalline and single crystals) and a deep eutectic solvent (DES) is investigated.
- Cyclic voltammograms show singular features and sharp peaks.
- Copper electrodeposition on a gold surface is preceded by the formation of a UPD monolayer.
- Copper UPD on Au(hkl) is structure sensitive.
- Copper UPD on Au(poly) and Au(hkl) is influenced by the presence of chloride from the DES.